PATENT SPECIFICATION (11) 1 601 123

1 601 123

(21) Application No. 31153/77 (22) Filed 25 Jul. 1977
(23) Complete Specification Filed 11 May 1978
(44) Complete Specification Published 28 Oct. 1981
(51) INT. CL.[3] C11D 10/02
(C11D 10/02 1/825 3/20)
(52) Index at Acceptance
C5D 6B10C 6B11D 6B12L 6B12M 6B12N3
6B15 6B4 6B5 6C9

(72) Inventors: GEOFFREY PHILIP SHERIDAN
LINDA CHRISTINE BODEN

(19)

(54) CLEANING COMPOSITIONS

(71) We, DIAMOND SHAMROCK INDUSTRIAL CHEMICALS LIMITED, formerly known as LANKRO CHEMICALS LIMITED, a British Company, of Emerson House, Albert Street, Eccles, Manchester, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be described in and by the following statement:-

This invention relates to cleaning compositions, and concerns in particular toilet cleaning compositions intended to be placed within the toilet cistern and of the type referred to as free-standing blocks.

It is known that toilets and urinals may be kept clean by placing in the cistern associated therewith a cleaning composition designed to dissolve in the water and thus to be released into and applied to the toilet or urinal upon the flushing thereof. The composition employed may be retained within a container to which the water in the cistern has limited access, but recently it has proved desirable to employ a free-standing block – that is to say, a composition which been produced in block or tablet form and which can be placed directly in the cistern without the use of any container.

For such free-standing blocks to work satisfactorily overall – it is expected that a standard-sized block (usually a 2 × 4 × 5 cms tablet weighing about 50g) will last for at least 30 days – they should necessarily be relatively water insoluble (hydrophobic), otherwise they simply dissolve completely away within hours of being placed in the cistern. However, it is also necessary, if such free-standing blocks are to have sufficient cleaning power, for at least the main active ingredient of the block to be water-soluble (hydrophilic). These conflicting requirements have so far been met by making the block of effectively two different components; one, the major component, is a hydrophobic carrier, while the other, the minor component, is a hydrophilic surfactant compatible with the first component. The two components (each of which can in fact be a mixture of materials) are additionally chosen so that each of them, and the composition formed by their admixture as melts, is solid at ambient temperature; commonly the two are actually mixed in the form of a melt which is cast into tablets or blocks. As stated above, the tablets or blocks are normally about 2 × 4 × 5 (cms), and weigh approximately 50g.

The free-standing tablet or block compositions presently available are in general fairly satisfactory, though they do suffer from a number of relatively minor drawbacks. For example, the components currently employed have to be mixed as a quite high temperature melt (about 90-100°C), which is wasteful of energy. Secondly, the proportions of the components presently used are in fact rather critical; even relatively minor changes therein can result in significant changes in the performance and/or water-stability of the product, and this makes bulk manufacture a little difficult. Thirdly, the components used at the moment as the main active ingredients – the hydrophilic surfactants – are not, in the context of the composition, particularly efficient.

We have now found that an improved composition, which does not suffer nearly so badly from the drawbacks mentioned above, can be obtained by the careful selection of the materials employed in the preparation of the composition.

In one aspect, therefore, this invention provides a cleaning composition suitable for use as or in the preparation of a toilet or urinal free-standing cleaning tablet or block, which composition comprises an intimate admixture of:

(a) as the hydrophobic carrier component, 100 parts by weight of a mixture of:-

(i) one or more fatty acid dialkanolamide, and
(ii) one or more alkoxylated fatty acid monoalkanolamide containing from 1 to 4 moles alkylene oxide per mole,

this mixture containing the two types of alkanolamide in a weight ratio of from 1:4 to 1:0.5 dialkanolamide (i): alkoxylated monoalkanolamide (ii);

(b) as the hydrophilic surface-active component, from 200 to 50 parts by weight of one or more ethylene oxide/propylene oxide copolymer which is based on a polypropylene glycol with a molecular weight of at least 1,000, contains at least 50 wt % ethylene oxide, and has a molecular weight of at least 4,000; and

(c) as a binder/plasticiser, from 1 to 40 parts by weight of one or more diester of an aryl or aliphatic dicarboxylic acid with one or two monohydric aliphatic alcohols.

The hydrophobic component, which is primarily present as a carrier but is nevertheless chosen to have a significant surface active effect, is a mixture of one or more fatty acid dialkanolamide with one or more alkoxylated fatty acid monoalkanolamide. The degree of hydrophobicity of this mixture naturally depends upon the hydrophobic nature of the individual constituents and upon the weight ratio of dialkanolamide to alkoxylated monoalkanolamide.

The fatty acid dialkanolamide may be any of those materials conventionally used, or suggested for use, as detergent foam stabilisers. Thus: the fatty acid moiety may be derived from a straight or branched, saturated or unsaturated organic carboxylic acid containing from 10 to 18 carbon atoms, typical such acids being decanoic, undecylenic, lauric, stearic, oleic and palmitic acids, or mixtures thereof, especially those mixtures known as tallow and coconut fatty acids; the alkanol moiety may be derived from a lower aliphatic alcohol having from 1 to 3 carbon atoms, typical such alcohols being ethanol and isopropanol. The commercially-available dialkanolamides are in general mixtures of related compounds, and the exact composition and hydrophobicity of any such mixture will depend upon the process by which it was made. Typical fatty acid dialkanolamides are the mixtures known as tallow- and (especially) coconut-diethanolamide. The latter is available under the name ETHYLAN LTD (ETHYLAN is a Registered Trade Mark).

The alkoxylated fatty acid monoalkanolamide is conveniently an alkoxylated version of one of the fatty acid monoalkanolamides also conveniently used, or suggested for use, as detergent foam stabilisers. Thus: the fatty acid moiety may be derived from a straight or branched, saturated or unsaturated organic carboxylic acid containing from 10 to 18 carbon atoms, typical such acids being decanoic, undecylenic, lauric, stearic, oleic and palmitic acids, or mixtures thereof, especially those mixtures known as tallow and coconut fatty acids; the alkanol moiety may be derived from a lower aliphatic alcohol having from 1 to 3 carbon atoms, typical such alcohols being ethanol and isopropanol; typical fatty acid monoalkanolamides are tallow- and (especially) coconut- monoethanolamide. The degree of alkoxylation is such as to give from 1 to 4 moles alkylene oxide per mole, preferably 2 moles per mole. Most conveniently the alkoxide is in fact ethylene oxide. A particularly preferred alkoxylated fatty acid monoalkanolamide is a 2 mole/mole ethoxylate of coconut monoethanolamide, which is available under the name ETHYLAN LM2.

The two alkanolamides provide the hydrophobic component of the compositions of the invention. However, since the alkoxylated alkanolamides are somewhat less hydrophobic than the others (depending on the degree of alkoxylation), the degree of hydrophobicity of the mixture of these two types can be varied by altering their weight ratio within the stated range of 1:4 to 1:0.5 dialkanolamide: alkoxylated monoalkanolamide. A preferred weight ratio range is from 1:2 to 1:0.5, and a particularly preferred ratio is 1:1.

The hydrophilic component, which is primarily responsible for the cleaning activity of the compositions, is one or more ethylene oxide/propylene oxide copolymer, preferably a block copolymer. This component is also a conventional nonionic surface active material. Conveniently it is based on a polypropylene glycol having a molecular weight of up to 2,500 (preferably 1,700), may contain up to 90 wt % ethylene oxide (preferably 80 wt %), and has a molecular weight of up to 12,000 (preferably 8,000). In practice, of course, the copolymers used are mixtures of materials which have the chosen figures as an average. A typical ethylene oxide/propylene oxide block copolymer is that sold under the name MONOLAN 8000E/80 (which has a molecular weight of 8,000, an ethylene oxide content of 80 wt %, and is based on a polypropylene glycol of molecular weight 1,700). (MONOLAN is a Registered Trade Mark).

The compositions of the invention contain from 200 to 50 parts by weight of ethylene oxide/propylene oxide copolymer per hundred parts alkanolamide mixture. Compositions containing more than 200 parts copolymer dissolve to readily, thus in use having too short a life, while compositions containing less than 50 parts copolymer have too low a setting point, thus being difficult to prepare in block or tablet form. Preferably the compositions contain from 150 to 50, especially 100 parts by weight of the copolymer per 100 parts by

weight alkanolamide mixture.

The third component of the compositions of the invention is the binder/plasticiser, which is one or more aryl or aliphatic dicarboxylic acid monohydric aliphatic alcohol diester. The preferred dicarboxylic acids used to form the diesters are those containing from 5 to 10 carbon atoms, especially the aryl dicarboxylic acids containing 8 carbon atoms or the aliphatic dicarboxylic acids containing from 6 to 10 carbon atoms. The particularly preferred dicarboxylic acids are phthalic acid (C_8), adipic acid (C_6), azelaic acid (C_9) and sebacic acid (C_{10}) or mixtures thereof. The preferred alcohols used to form the diesters are the saturated monohydric alcohols containing from 1 to 8 carbon atoms, such as ethanol and butanol. Particularly preferred binder plasticisers are the dialkyl phthalates, especially dibutyl phthalate.

The amount of binder/plasticiser phthalate used in the compositions of the invention is from 1 to 40 parts by weight per 100 parts by weight hydrophobic component. Compositions containing less than 1 part are too short lived, tending to fall apart too easily, whilst compositions containing more than 40 parts tend to be too soft, thus causing handling problems during manufacture. Preferred amounts of binder/plasticiser are from 5 to 20, especially 12, parts by weight per 100 parts by weight alkanolamide mixture.

Though the compositions so far defined are very satsifactory, they may for some purposes be rather expensive. Accordingly, in order to reduce their cost they may incorporate up to 100 parts by weight per 100 parts by weight hydrophobic component of one or more filler (though it will be appreciated that the use of large amounts of filler may significantly alter the physical characteristics of the blocks made from such compositions). The filler may be any of those conventionally used, or suggested for use, in cleaning compositions – and may thus be one or more inorganic sulphate, phosphate, polyphosphate, carbonate and silicate, and starch. A typical filler is in fact a starch of the grade known as "Snowflake acid-thinned" starch. (SNOWFLAKE is a Registered Trade Mark).

The compositions of the invention may, of course, contain other ingredients – such as bactericides or bacteriostats, dyes and perfumes – provided they do not, in the quantities used, significantly and detrimentally affect the compositions. In general these additional ingredients will be present in fairly small amounts (say, from 1 to 15 parts by weight per 100 parts by weight alkanolamide mixture). Typical bioactive materials are benzalkonium chloride, cetyl pyridinium chloride (CETRIMIDE) and halo-o-hydroxydiphenyls (such as IRGASAN DP 300) in amounts of 7 or 8 parts per 100 parts, a typical deodorising material is para-dichloro-benzene in amounts of 7 or 8 parts per 100 parts, while a suitable dyestuff is Erio Brilliant Blue V, useful in amounts of 7 or 8 parts per 100 parts. (IRGASAN is a Registered Trade Mark).

In order to prepare the compositions of the invention the various ingredients may simply be mixed together with gentle heating to about 60°C to form a melt, this melt then conveniently being cast into tablets or blocks of an appropriate size and shape. The formed tablets or blocks may if desired be wrapped (to avoid moisture pick-up), and losses due to evaporation), and the wrapping may conveniently be a water-soluble film – made from a synthetic resin such as polyvinyl alcohol, for example – to obviate any need for the block to be unwrapped before being placed in position.

The following Examples are now given, though only by way of illustration, to show details of various embodiments of the invention.

Example 1:

Toilet blocks having the following constitution were prepared as described.

Hydrophobic components

ETHYLAN LM 2 (a 2 mole/mole coconut monoethanolamide ethoxylate)	50g
ETHYLAN LD (a coconut diethanolamide)	50g

Hydrophilic component

MONOLAN 8000 E/80 (an ethylene oxide/propylene oxide block copolymer)	100g

Binder/plasticiser

Dibutyl phthalate	12g

Dyestuff

Erio Brilliant Blue V	8g

50 gms of the 2 mole/mole coconut monoethanolamide ethoxylate (ETHYLAN LM2) were mixed with 50 gms of the coconut diethanolamide (ETHYLAN LD), and the whole was heated to 60°C in a suitable vessel. 100 gms of MONOLAN 8000 E/80 (an ethylene oxide/propylene oxide block copolymer based on a polypropylene glycol having a molecular weight 1,700; it has an ethylene oxide content of 80% and a total molecular weight of 8000)

were added, and the mixture was agitated until the MONOLAN dissolved therein. 12 gms of dibutyl phthalate were then added and stirred in until dissolved. Finally, 8 gms of the Erio Brilliant Blue V dyestuff were charged, and the whole agitated until the dyestuff was completely dissolved.

The composition was then individually moulded into tablets of convenient size and weight (2×4×5 cms and 50 gms), and allowed to set. The formed tablets were wrapped to avoid moisture pick-up or losses due to evaporation.

A number of tablets formed as described were placed in position in flush lavatory cisterns. They all lasted for at least 30 days, exhibiting cleaning ability throughout.

Examples 2-10

In the same way there were prepared a number of similar cleaning compositions (as shown in the Table below), from which tablets were formed. All the tablets gave satisfactory cleaning performance for at least 30 days. The figures are amounts in parts by weight.

The composition of Example 1 is also included in the Table.

TABLE

	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
Hydrophobic components										
ETHYLAN LM 2	50	50	50	75	50	50	50	50	50	50
ETHYLAN LD	50	50	50	25	50	50	50	50	50	50
Hydrophilic components										
MONOLAN 8000 E/80	100	150	75	200	200	100	150	150	-	200
MONOLAN 12000 E/80	-	-	-	-	-	-	-	-	150	-
Plasticiser/binder										
Dibutyl phthalate	12	12	12	12	20	5	-	-	12	12
Diethyl phthalate	-	-	-	-	-	-	20	-	-	-
Dioctyl phthalate	-	-	-	-	-	-	-	7.5	-	-
Other components										
Dyestuff (Erio Brilliant Blue V)	8	8	8	10	10	8	8	8	8	10
p-Dichlorobenzene	-	-	-	-	-	-	-	-	-	8

ETHYLAN LM 2, ETHYLAN LD and MONOLAN 8000 E/80 are described above.
MONOLAN 1200 E/80 is an ethylene oxide/propylene oxide block copolymer based on a polypropylene glycol of molecular weight 2,400; it has an ethylene oxide content of 80% and a total molecular weight of 12,000.

Example 11

Toilet blocks having the following composition (the amounts are parts by weight) were prepared as described.

Hydrophobic components	
ETHYLAN LM 2	50
ETHYLAN LD	50
Hydrophilic component	
MONOLAN 8000 E/80	150
Binder/PLASTICISER	
Dibutyl phthalate	12
Filler	
Snowflake acid-thinned starch	100
Dyestuff	
Erio Brilliant Blue V	10
De-odorant	
p-dichlorobenzene	8

The composition was prepared in the same manner used for the composition of Example 1, the filler being stirred in after the addition and dissolution of the dibutyl phthalate.

Tablets were prepared from the formed composition using the method described in Example 1. They were tested by being placed in flush lavatory cisterns, and all exhibited satisfactory cleaning ability for at least 30 days.

WHAT WE CLAIM IS:

1. A cleaning composition, suitable for use as or in the preparation of a toilet or urinal free-standing tablet or block, comprising an intimate admixture of:
   (a) as the hydrophobic carrier component, 100 parts by weight of a mixture of:-
      (i) one of more fatty acid dialkanolamide, and
      (ii) one or more alkoxylated fatty acid monoalkanolamide containing from 1 to 4 moles alkylene oxide per mole,
   this mixture containing the two types of alkanolamide in a weight ratio of from 1:4 to 1:0.5 dialkanolamide (i): alkoxylated monoalkanolamide (ii);
   (b) as the hydrophilic surface-active component, from 200 to 50 parts by weight of one or more ethylene oxide/propylene oxide copolymer which is based on a polypropylene glycol with a molecular weight of at least 1,000, contains at least 50 wt% ethylene oxide, and has a molecular weight of at least 4,000; and
   (c) as a binder/plasticiser, from 1 to 40 parts by weight of one or more diester of an aryl or aliphatic dicarboxylic acid with one or two monohydric aliphatic alcohols.

2. A composition as claimed in claim 1, wherein the fatty acid moiety of the fatty acid dialkanolamide is derived from a straight or branched, saturated or unsaturated organic carboxylic acid containing from 10 to 18 carbon atoms.

3. A composition as claimed in claim 2, wherein the fatty acid moiety is derived from any of decanoic, undecylenic, lauric, stearic, oleic and palmitic acids or mixtures thereof.

4. A composition as claimed in any of the preceding claims, wherein the alkanol moiety of the fatty acid dialkanolamide is derived from a lower aliphatic alcohol having from 1 to 3 carbon atoms.

5. A composition as claimed in claim 4, wherein the aliphatic alcohol is ethanol or isopropanol.

6. A composition as claimed in any of the preceding claims, wherein the fatty acid dialkanolamide is tallow- or coconut-diethanolamide.

7. A composition as claimed in any of the preceding claims, wherein the fatty acid and alkanol moieties of the alkoxylated fatty acid monoalkanolamide are as defined in any of claims 2 to 6 in respect of the fatty acid dialkanolamide.

8. A composition as claimed in claim 7, wherein the degree of alkoxylation of the alkoxylated fatty acid monoalkanolamide is such as to give 2 moles of alkylene oxide per mole of fatty acid monoalkanolamide.

9. A composition as claimed in either of claims 7 and 8, wherein the alkoxylated fatty acid monoalkanolamide is an ethoxylated fatty acid monoalkanolamide.

10. A composition as claimed in any of claims 7 to 10, wherein the alkoxylated fatty acid monoalkanolamide is a 2 mole/mole ethoxylate of coconut monoethanolamide.

11. A composition as claimed in any of the preceding claims, wherein the weight ratio of fatty acid dialkanolamide to alkoxylated fatty acid monoalkanolamide is from 1:2 to 1:0.5.

12. A composition as claimed in claim 11, wherein the weight ratio is 1:1.

13. A composition as claimed in any of the preceding claims, wherein the ethylene oxide/propylene oxide copolymer is a block copolymer.

14. A composition as claimed in any of the preceding claims wherein the ethylene oxide/propylene oxide copolymer is based on a polypropylene glycol having a molecular weight of up to 2,500.

15. A composition as claimed in claim 14, wherein the polypropylene glycol has a molecular weight of 1,700.

16. A composition as claimed in any of the preceding claims wherein the ethylene oxide/propylene oxide copolymer contains up to 90% by weight of ethylene oxide.

17. A composition as claimed in claim 16, wherein the ethylene oxide/propylene oxide copolymer contains 80% by weight of ethylene oxide.

18. A composition as claimed in any of the preceding claims wherein the ethylene oxide/propylene oxide copolymer has a molecular weight of up to 12,000.

19. A composition as claimed in claim 18, wherein the ethylene oxide/propylene oxide copolymer has a molecular weight of 8,000.

20. A composition as claimed in any of the preceding claims, which contains from 150 to 50 parts by weight of ethylene oxide/propylene oxide copolymer per hundred parts of alkanolamide mixture.

21. A composition as claimed in claim 20 which contains equal parts by weight of copolymer and alkanolamide mixture.

22. A composition as claimed in any of the preceding claims, wherein the dicarboxylic acid-derived portion of the dicarboxylic acid aliphatic alcohol diester binder/plasticiser component is based on an aryl dicarboxylic acid containing 8 carbon atoms or an aliphatic dicarboxylic acid containing from 6 to 10 carbon atoms.

23. A composition as claimed in claim 22, wherein the dicarboxylic acid is any of phthalic, adipic, azelaic and sebacic acids, or mixtures thereof.

24. A composition as claimed in any of the preceding claims, wherein the aliphatic alcohol-derived portion of the dicarboxylic acid aliphatic alcohol diester binder/plasticiser component is based on a saturated monohydric alcohol containing from 1 to 8 carbon atoms.

25. A composition as claimed in claim 24, wherein the alcohol is ethanol or butanol.

26. A composition as claimed in any of the preceding claims, wherein the binder/plasticiser component is a dialkyl phthalate.

27. A composition as claimed in claim 26, wherein the binder/plasticiser component is dibutyl phthalate.

28. A composition as claimed in any of the preceding claims, wherein the binder/plasticiser component is used in an amount of from 5 to 20 parts by weight per 100 parts by weight of the hydrophobic component.

29. A composition as claimed in claim 28 wherein the binder/plasticiser component is used in an amount of 12 parts by weight per 100 parts by weight of the hydrophobic component.

30. A composition as claimed in any of the preceding claims, and substantially as described hereinbefore with reference to any of the Examples.

31. A composition as claimed in any of the preceding claims which is in the form of a block and is wrapped in a water soluble film which may be left in position on the block in its end use.

J.P.L. HOOPER
Agent for the Applicants
Lankro Chemicals Limited.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1981.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.